Molecular Engineering of Conjugated Polymers for Solar Cells: An Updated Report

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The device efficiency of polymer:fullerene bulk heterojunction solar cells has recently surpassed 11%, as a result of synergistic efforts among chemists, physicists, and engineers. Since polymers are unequivocally the "heart" of this emerging technology, their design and synthesis have consistently played the key role in the device efficiency enhancement. In this article, the first focus is a discussion on molecular engineering (e.g., backbone, side chains, and substituents), then the discussion moves on to polymer engineering (e.g., molecular weight). Examples are primarily selected from the authors contributions; yet other significant discoveries/developments are also included to put the discussion in a broader context. Given that the synthesis, morphology, and device physics are inherently related in explaining the measured device output parameters (J_{sc}, V_{oc} and FF), we will attempt to apply an integrated and comprehensive approach (synthesis, morphology, and device physics) to elucidate the fundamental, underlying principles that govern the device characteristics, in particular, in the context of disclosing structure-property correlations. Such correlations are crucial to the design and synthesis of next generation materials to further improve the device efficiency.

1. Introduction

It is not exaggerating to state that tremendous progress has been achieved for conjugated polymer-based solar cells in the years since we published our last comprehensive review in 2012.[1] The power conversion efficiency (η) – the percentage of solar light input converted into usable electricity output – has reached ≈12% in academic labs,[2] making polymer solar cells a serious contender to the much more established amorphous silicon solar cells (≈13%).[3] This triumph is a result of synergistic efforts among chemists, physicists, and engineers, a true testimony to the necessity of having interdisciplinary approaches to tackle complex problems.

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DOI: 10.1002/adma.201601391

A polymer solar cell, typically consisting of a polymer:fullerene blend in a bulk heterojunction (BHJ) configuration for converting light into electricity, is a complex system. Though the material properties of the active layer (i.e., optoelectronic properties of polymers and fullerenes) set the upper limit on the output of the photovoltaic device (i.e., the efficiency), many other factors need to be optimized and function synergistically to maximize the device characteristics (i.e., short circuit current, J_{sc}; open circuit voltage, V_{oc}; and the fill factor, FF) within the upper limit. The intrinsic complexity of BHJ solar cells thus requires a variety of expertise in synthesis, morphology, and device physics (including physical chemistry). A rough relationship of these expertise is presented in **Figure 1**. Design and synthesis of materials has primarily focused on the polymers, given that there is a limited amount of functionalization one can apply to the synthesis of fullerenes.[4] Still, there are numerous factors one must consider in the synthetic design of these polymers. From a molecular engineering point of view, choosing the right conjugated repeating unit decides the energy levels and the band gap; selecting the appropriate side chains largely determines the solubility in the processing solvent; both conjugated backbone and the side chains have a significant impact on the aggregation and intermolecular interactions in the active layer. From a polymer engineering point of view, one needs to carefully balance the molecular weight, dispersity, solubility in the processing solvents, and viscosity of the resulting solution (i.e., the "active ink"). The polymer:fullerene blend in a processing solvent, the "active ink", then goes through one of several solution-processing methods (e.g., spin coating, slot-die, doctor-blading, etc.), to become a thin film (i.e., the active layer) that (ideally) has the optimal morphology to maximize the device output. Given the significance of the morphology, a variety of methods have been applied to control the kinetically trapped morphology of the active layer, including weight ratio of polymer vs fullerene, processing additives,[5] solvent annealing,[6] and thermal annealing,[7] among others. However, the optimal morphology for a given BHJ blend for reaching the maximum device characteristics is largely materials dependent; thus fundamentally understanding and characterizing the morphology, in particular, correlating morphological features with the device

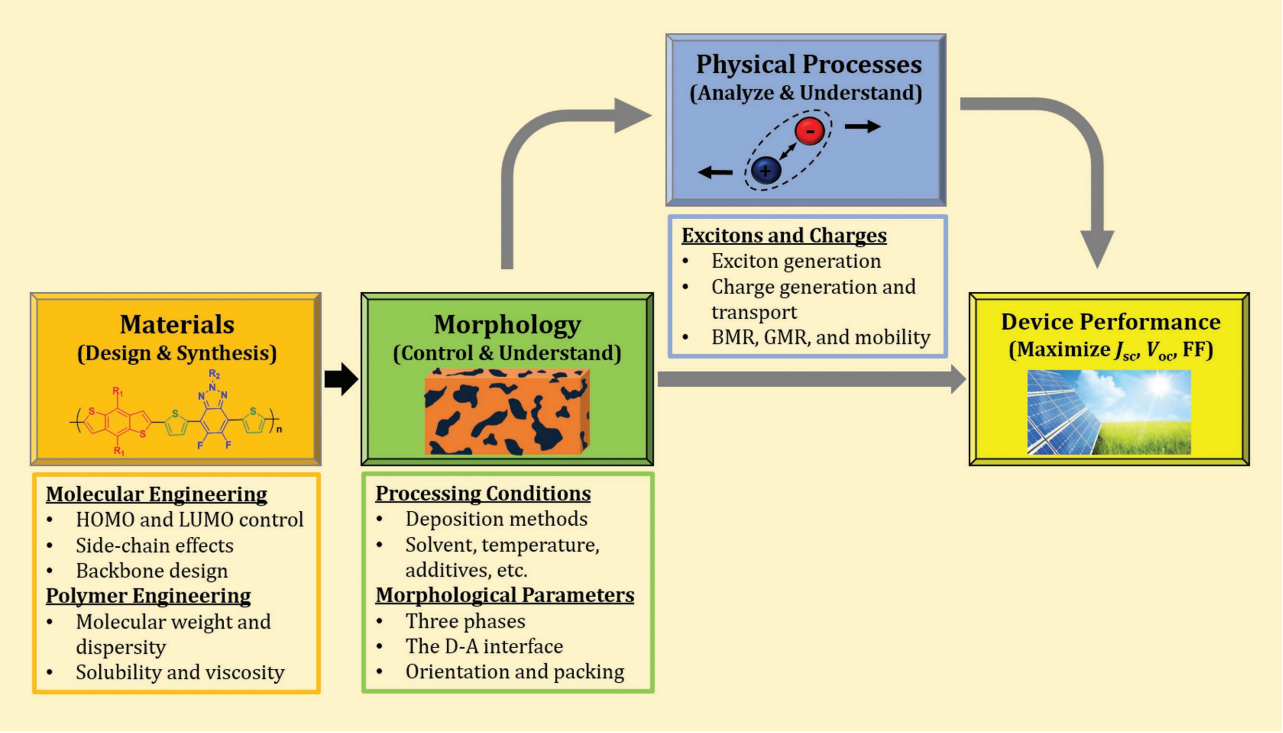

Figure 1. A rough relationship of key elements/required expertise in polymer solar cells: synthesis, morphology, and device physics are tightly related, with the ultimate goal of maximizing the efficiency. Materials and processing together will determine the morphology, the morphology would determine the "actual input" (e.g., band gap, energy levels, aggregation state) into the device physics; analyzing and understanding the device physics, will provide direct explanation of the observed device performance.

characteristics (J_{sc}, V_{oc}, and FF), becomes increasingly important. Finally, the materials properties and morphological features of the active layer determine the fundamental optical and electronic processes in such a thin film, including exciton generation and separation, charge generation, transport, collection, and recombination, all of which offer direct and quantitative insights into the device performance. Thus, analyzing and understanding these device-related physical processes is a key piece to a comprehensive understanding of the relationship between the structures (of materials) and properties (of devices).

Here, we will focus on the novel design and synthesis of conjugated polymers that have emerged in the years since our last review.[1] The key design principles (e.g., "weak donor-strong acceptor") for constructing the conjugated backbone still hold;[8] however, we have obtained further understanding of these design principles with deliberately designed materials systems, primarily through applying morphological characterization and device physics to these systems (Figure 1). We will first focus our discussion on the molecular engineering (e.g., backbone, side chains, and substituents), then move on to polymer engineering (e.g., molecular weight). Examples will be primarily selected from our own contributions; yet other significant discoveries/developments will also be included to put the discussion in a broader context. Given that synthesis, morphology, and device physics are inherently related in explaining the measured device output parameters (J_{sc}, V_{oc} and FF), we will attempt to apply an integrated and comprehensive approach (synthesis, morphology, and device physics) to elucidate the fundamental underlying principles that govern the device characteristics, in particular, in the context of disclosing structure–property correlations. Such correlations are crucial to the design and synthesis of next generation materials to further improve the device efficiency.

2. Molecular Engineering (Backbone, Substituents, and Side Chains)

From the molecular engineering point of view, the conjugated polymers for solution-processed BHJ solar cells typically have three constituting structural components: conjugated backbone, side chains, and often, substituents (**Figure 2**a) We separately list substituents because they often exert interesting (sometimes significant) impacts on the BHJ system, which cannot be solely explained by their electronic influence (e.g., electron donating/withdrawing) to the conjugated backbone. Among the three components, the conjugated backbone is unequivocally the primary factor in dictating the intrinsic optoelectronic properties of conjugated polymers, including energy levels, band gap, mobilities, etc. However, side chains (and substituents) also have sizable influence on the optoelectronic properties of these conjugated polymers, in particular, in the solid state where the morphological features (aggregation, packing/stacking, etc.) are significantly affected by the choice of side chains (and substituents).

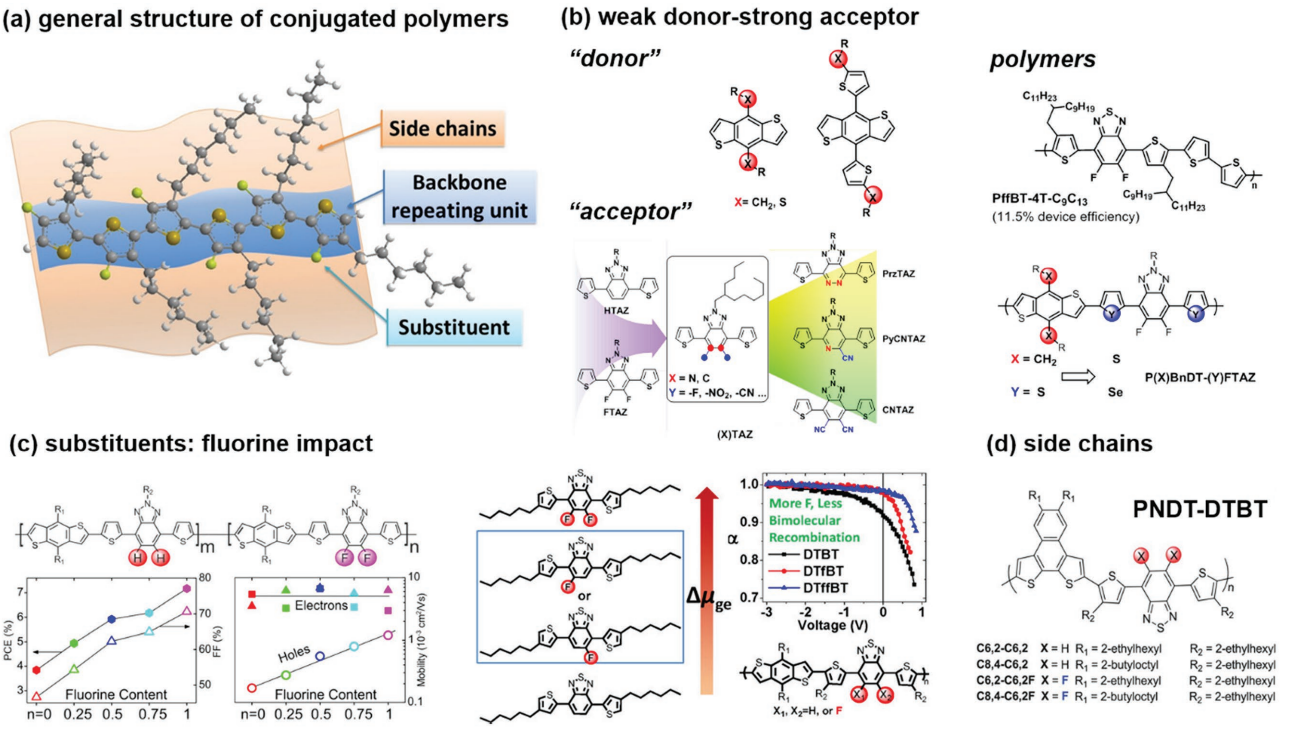

Figure 2. (a) The three constituents to conjugated polymers. Reprinted with permission;[1] copyright 2012 American Chemical Society. (b) recent developments in donor moieties and acceptor moieties, and representative polymers. Reprinted with permission.[11c,17] Copyright 2014, 2015 American Chemical Society. (c) Two detailed studies exploring the fluorine impact. Reprinted with permission.[23,24] Copyright 2013, 2014 American Chemical Society. (d) one example disentangling the influence of side chains and fluorine substitutions. Reproduced with permission.[27] Copyright 2013, Royal Society of Chemistry.

2.1. Backbone

Since the "weak donor-strong acceptor" approach can fine-tune the energy levels and band gaps of conjugated polymers (almost) independently,[8] it has been widely adopted in the design of conjugated backbones. On the donor front, fused aromatics are dominating the stage, due to their benefits which include minimized steric hindrance between adjacent conjugated units, tunable HOMO levels, and increased stacking/packing in the solid state (thus a higher charge carrier mobility), among others. However, excessively fused aromatics have introduced issues such as their significantly decreased solubility in processing solvents, in addition to the synthetic difficulties in obtaining highly fused aromatics with properly decorated side chains.[9] Balancing the "investment vs return," it is not surprising that the majority of such fused aromatics have been a rather straightforward fusion of three or four simple aromatics, for example, benzodithiophene (BnDT), which is perhaps the most popular fused aromatic in the design of conjugated polymers for solar cells.[10] A few notable modifications to the basic structure of BnDT that have emerged recently are briefly discussed here. First, connecting the alkyl side chains to the center benzene of BnDT via a sulfur atom can noticeably increase the V_{oc} of such polymer based BHJ devices to ≈0.9 V, an effect that has not been sufficiently understood.[11] Second, adding an extra (alkylated) thiophenyl unit on each side of the center benzene of BnDT appears to boost the J_{sc} of related BHJ devices,[12] possibly due to the two-dimentional transport pathway (from the additional conjugation on the side chains) that can improve the hole transport. The most recent advance is to combine these two strategies, i.e., adding the alkylthio side chains to these two thiophenyl units on the center benzene of BnDT. A few polymers based on this new version of BnDT[13] have shown device efficiencies up to 9.52%,[13b] with a V_{oc} of 0.807 V, a J_{sc} of 17.55 mA cm^{-2}, and a FF of 0.672.

On the acceptor front, a few fused aromatics have also gained popularity and shown impressive device performance with their polymers, including FTT,[14] DPP,[15] isoindigo,[16] DTffBT,[10b] and FTAZ (Figure 2b).[10d] The most recent advance in the design and synthesis of novel acceptors is perhaps the discovery of a few new electron deficient triazole units (Figure 2b). Specifically, Li et al. designed a general strategy to create three new electron deficient triazole units and synthesized three new polymers by combining them with BnDT.[17] One new polymer, PyCNTAZ, was able to offer an overall device efficiency of 8.4% with both V_{oc} and J_{sc} higher than those of the original PBnDT-FTAZ based devices at a thickness of ≈300 nm.

Another notable development is the introduction of non-common heteroatoms for aromatics (e.g., Ge, Si, Se) into the conjugated backbone. Perhaps the most successful strategy is to replace the sulfur (S) (for example, in thiophene) with selenium (Se). For example, replacing the thiophene units in the conjugated backbone with selenophene can noticeably lower the band gap of conjugated polymers (mainly through lowering the LUMO level), which could lead to a higher J_{sc} in the device output, as Uy et al. observed.[11c] However, in their case study,

the overall efficiency of the selenophene polymer based device was lower than that of the thiophene based counterpart, due to diminished V_{oc} and FF in the former. Though the majority of the published reports investigated the substitution of thiophene with selenophene or even tellurophene,[18] some attempted a similar strategy in engineering the acceptors, for example, by replacing the sulfur in the benzothiadiazole unit with selenium/tellurium.[19] The Hsu group conducted studies comparing the fluorinated benzoselenadiazole[20] with the fluorinated benzothiadiazole.[21] They observed a higher J_{sc} in the former polymer based devices whereas the overall efficiency was higher for the latter. To conclude the discussion on the effect of heteroatoms in the conjugated backbone, we want to point to a comprehensive study that exhaustively explored the substitution of selenium on the conjugated backbone.[22] In that report, Jiang et al. varied the location and number of selenium atoms in 2D conjugated polymers and explored the effect of selenium substitution on energy levels, band gaps, and related device performance.

Finally, we want to remind the readers that though the electron-withdrawing nature of these acceptors primarily determines the LUMO energy level of such "donor–acceptor" conjugated polymers, the acceptor has some influence on the HOMO energy level of the "donor–acceptor" conjugated polymer as well (similarly, the donor moiety also has some impact on the LUMO energy level of the polymer). Therefore, one can only – semi-empirically – estimate the energy levels and the band gap of a "donor–acceptor" conjugated polymer having known donor and acceptor moieties; the exact values of these energy levels have to be experimentally determined (e.g., via a combination of cyclic voltammetry and UV–Vis absorption profile).

2.2. Substituents

Many substituents, strictly speaking, are an integral part of the conjugated backbone due to their participation in the conjugation; we arbitrarily single them out because they often exert similar electronic impact on different conjugated units, and sometimes their influence extends beyond the electronic impact. For example, electron-rich substituents (e.g., alkoxy) can elevate the energy level of the conjugated backbone, whereas electron-withdrawing ones (e.g., cyano) can lower the energy level. Thus the substituents offer additional control/tuning of the energy levels and the band gap of conjugated polymers. On the other hand, some substituents, for example, fluorine, can not only exert the expected electron-withdrawing effect to the conjugated backbone, but also – perhaps more importantly – have a profound impact on the morphology and charge/exciton related physical processes in the BHJ film. We carried out two comprehensive studies on this peculiar "fluorine" effect based on our two previously published systems, PBnDT-DTffBT,[10b] and PBnDT-FTAZ.[10d] In one study, Stuart et al. introduced PBnDT-DTfBT ("1F") to accompany PBnDT-DTBT ("0F") and PBnDT-DTffBT ("2F").[23] With these three structurally similar polymers (only differing on the number of fluorine substitutions on the benzothiadiazole), and by applying various experimental and computational methods, Stuart et al. showed that adding fluorine atoms to the conjugated backbone can noticeably enhance all three key parameters of the device output (V_{oc}, $J_{sc,}$ and FF) for a variety of reasons. While the increase of V_{oc} can be largely ascribed to the suppressed HOMO level by the increased fluorine substitution, the improvement of J_{sc} and FF with more fluorine substituents is a rather synergistic effect of desirable morphological features and beneficial exciton/charge behaviors. For example, the "2F" polymer shows enhanced face-on orientation and improved π–π stacking in its BHJ blend with PCBM (a fullerene derivative), both of which are desirable features to promote charge transport. The observed larger polymer/fullerene domains with high purity in the case of the "2F" polymer would likely explain the reduced bimolecular recombination (observed via photocurrent vs light intensity study). On the other hand, the larger $\Delta\mu_{ge}$ (change of the dipole moment from the ground state to the excited state) associated with the increased amount of fluorine substituents implies that the geminate recombination is also hindered by the increased fluorination. All these contribute to the significant device efficiency enhancement from 4% in the case of the "0F" polymer to 7% for the "2F" polymer. In another study, Li et al. systematically increased the fluorine content with a series of five PBnDT-(X)TAZ based copolymers.[24] After identifying that device efficiency tracks the FF exceedingly well, both of which monotonically increase with the increasing fluorine content, Li et al. conducted a comprehensive study on both morphology and device physics of these BHJs. What is striking from this study is that a single parameter, the hole mobility, is responsible for the change of FF in these solar cells of thick active layers (over 300 nm). The monotonic increase of hole mobility with the increased fluorine content benefits faster charge extraction, which eventually results in an impressive FF of 72% in the case of the F100 (i.e., PBnDT-FTAZ) based device. These two detailed studies represent the latest understanding of the "fluorine" impact; yet their different explanations indicate that the device efficiency enhancement gained by adding these fluorine substituents could be materials system dependent. Nevertheless, more studies are definitely needed to further understand the "fluorine" impact, in particular, because the key constructing unit of the polymer having the record-high efficiency (11.5%) is DTffBT.[2]

2.3. Side Chains

In our early studies, we demonstrated that the position of these side chains on the conjugated backbone has a strong impact on the band gap of the conjugated polymers, primarily due to the steric hindrance induced twist in the adjacent conjugated units;[25] more importantly, we further revealed that the shape and size of the alkyl side chains has a profound impact in modulating the intermolecular interaction within the BHJ blend in the solid state, which has a direct impact on the device characteristics (V_{oc}, J_{sc} and FF).[26] In another study, Yang et al. designed a series of four polymers with an identical backbone but different combinations of side chains and fluorine substituents. As expected, both side chains and fluorine substitution can strongly impact the morphology and structural order in BHJ thin films.[27] It was rather pleasing to observe that the highest efficiency in this series of polymer-based devices

was obtained with the polymer that has the bigger side chains and fluorine substitution (C8,4-C6,2F in Figure 2d). Both a high V_{oc} and a high J_{sc} were obtained with this polymer-based device, rather than there being a trade-off between V_{oc} and J_{sc}, a dilemma from the earlier study.[26]

It has been generally accepted that one must achieve an optimized morphology in order to reach the highest possible device efficiency for any given polymer. Since these side chains can significantly influence the morphological parameters of the BHJ blend in the solid state (via carefully controlled processing conditions), the engineering of side chains has increasingly become an important approach to maximize the device efficiency for a given conjugated polymer.[28] Various research groups have made important contributions on this front, for example, the Takimiya group,[29] and the Yan group.[30] In fact, the polymer that has achieved the record-high device efficiency (PffBT4T-C_9C_{13} in Figure 2b) was structurally similar to the polymers in an earlier comprehensive investigation from the same group.[30]

To conclude this section, it is clear that structurally optimizing the conjugated polymer to achieve highest possible device efficiency is a very complex process, often guided by trial-and-error; a small structural perturbation to the existing conjugated polymer can indeed improve certain device characteristics (V_{oc}, J_{sc}, or FF), but other desirable properties may be compromised in the meantime.

3. Polymer Engineering

Molecular weight is perhaps the single most important parameter for polymers. To demonstrate the desirable macroscopic properties of any given polymer, a threshold molecular weight (for chain entanglement) has to be reached.[31] Conjugated polymers are no exception. While the band gap and energy levels of a conjugated polymer only require a few repeating units to be fully demonstrated, a number of carefully carried out studies[32] have provided conclusive evidence of the importance of a high, yet appropriate, molecular weight to obtain the highest device efficiency. For example, with carefully purified monomers and catalyst, and optimized reaction conditions, Li et al. were able to precisely control the molecular weight of PBnDT-FTAZ by applying the classical Carothers equation[32a] (**Figure 3**a). The highest device efficiency (7.3%) was obtained with the polymer having a molecular weight of 40 kg mol^{-1} (i.e., 40k polymer in Figure 2a). Though multiple explanations have been proposed to explain the molecular weight-dependent device performance, Li et al. showed that the compositional morphology (i.e., domain spacing and domain purity) was primarily responsible for the observed impact of the molecular weight on the device performance. Interestingly, the "recreated" 40k polymer (recreated by blending the 10k polymer and the 60k polymer) offered the second highest device efficiency in the studied series, yet there are subtle differences in

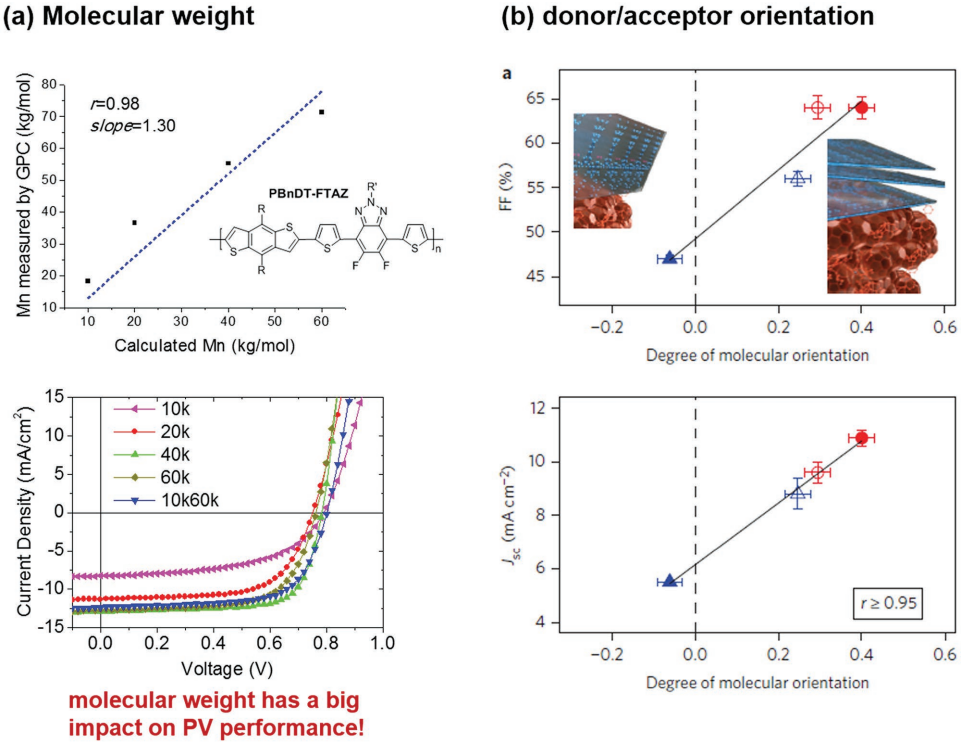

Figure 3. (a) Controlling the molecular weight of PBnDT-FTAZ and its impact on the device performance. Reproduced with permission.[32a] (b) The degree of molecular orientation to the donor/acceptor heterointerfaces, (+1) for perfect face-on and (–1) for perfect edge-on, has a strong correlation with the device characteristics. Reprinted with permission.[35] Copyright 2014, Nature Publishing Group.

device characteristics, morphology, and structure in the BHJ thin films, between the "recreated" 40k polymer (with a dispersity of 3.17) and the as-synthesized 40k polymer (with a dispersity of 2.15). This implied that the dispersity could play an important role in affecting the device performance. A recent study on the effect of dispersity on the device performance confirmed this hypothesis,[33] though the significant structural defects present in the polymers having large dispersity were cited as the culprit. Further study on dispersity is still necessary to truly understand its impact.

As stated above, a sufficiently high molecular weight is (almost) a prerequisite to fully demonstrate the true device behavior of a given conjugated polymer for solar cells; then the question is, is there any universally applicable "threshold" molecular weight for conjugated polymers (for solar cells)? Unfortunately, we believe the "threshold" molecular weight is dependent on the specific conjugated polymer, according to available literature reports (a few have been cited above[32]). Nevertheless, we suggest a minimum molecular weight of 20 kg mol^{-1} as the empirical "threshold" for conjugated polymers (for solar cells), which would correspond to ≈20 repeating units. Please note that it would be preferred to acquire the molecular weight with a high temperature GPC (gel permeation chromatography) system running a good solvent for conjugated polymers, since room temperature and non-ideal solvent could lead to severe aggregation of conjugated polymers and a false "positive" for a high molecular weight.

4. Morphology and Device Physics

Up to this point, it should become clear that maximizing the device performance requires an optimized thin film morphology, which is not only dependent on molecular structure, but also manipulated by the processing conditions. Furthermore, as discussed earlier, device physics offers fundamental insights into the physical processes within the thin film based device; all these exciton/charge related behaviors depend upon both molecular structure and thin film morphology (Figure 1). We will briefly discuss the recent progress on both fronts.

In terms of morphology, additional evidence collected in the past five years points to the presence of a donor–acceptor mixed domain where the exciton splitting/charge generation mainly occurs. Thus the originally believed interpenetrated biphasic model of distinctive donor domains and acceptor domains in the BHJ blend has been largely superseded by the three phase morphology that comprises an intermixed phase in addition to a (relatively) pure donor phase and a (relatively) pure acceptor phase.[34] In terms of structural order, the most recent discovery is that the molecular orientation relative to donor/acceptor heterointerface is an important parameter in realizing high BHJ device performance, which has been experimentally verified (Figure 3b).[35]

In terms of device physics, much progress has been made on further understanding the origin of V_{oc}, in particular, with works by Vandewal et al.[36] Sufficient experimental evidence and theoretical work suggest that V_{oc} is primarily determined by the interfacial charge-transfer (CT) states between the donors (i.e., conjugated polymers) and the acceptors (i.e., fullerene derivatives), and can be related with radiative emission and nonradiative recombination by Equation (1).

$$\begin{aligned} V_{oc} &= \frac{kT}{q} ln\left(\frac{J_{ph}}{J_0}+1\right) \\ &= \frac{E_{CT}}{q}+\frac{kT}{q} ln\left(\frac{J_{sc}h^3c^2}{fq2\pi(E_{CT}-\lambda)}\right) \\ &\quad +\frac{kT}{q} ln\left(EQE_{EL}\right) \end{aligned} \tag{1}$$

Details on this equations can be found in the references.[36a] Equation (1) indicates there are two energy loss (also V_{oc} loss) channels. The first is the loss due to radiative emission, $q\Delta V_{oc,\,rad} = -kT\,ln\left(\frac{J_{sc}h^3c^2}{fq2\pi(E_{CT}-\lambda)}\right)$, which is unavoidable. The second is the loss due to nonradiative recombination, $q\Delta V_{oc,\ nonrad} = -kT\,ln(EQE_{EL})$, which is, in principle, avoidable. For a typical polymer:fullerene based solar cell, the total loss ($q\Delta V_{oc}$) is ≈0.6 eV, with ≈0.25 eV loss from the radiative emission via CT states, and ≈0.35 eV loss due to nonradiative recombination. Additionally, E_{CT} is typically smaller than the optical band gap of the conjugated polymer (or fullerene derivative) by another 0.2 eV or larger. If the "avoidable" loss due to nonradiative recombination could be minimized by reducing the nonradiative recombination pathways, the V_{oc} would receive a significant boost (up to 0.35 V). This much improved V_{oc} would translate into an efficiency enhancement of 40% or more (if J_{sc} and FF were not changed). For example, the current record high efficiency of 12% would become 15%. Therefore, understanding the charge recombination mechanism, in particular, the energy loss due to bimolecular recombination,[37] has consistently been actively investigated. Furthermore, it becomes increasingly clear that high charge carrier mobilities (balanced for both electrons and holes) are required to achieve high FF of polymer solar cells.[38]

5. Conclusions and Outlook

Impressive progress has been made in molecularly engineering conjugated polymers toward high efficiency solar cells in the past five years, highlighted by the recently reported record high efficiency (11.5%) – a feat that has far exceeded the previous goal of 10% set in 2006 by Scharber et al.[39] However, as one can tell from Figure 2, this impressive accomplishment is achieved via a meticulous optimization of the molecular structure with known strategies, assisted by excellent morphological control via processing conditions. Strictly speaking, there have been essentially no uniquely designed building blocks, or novel design rationale that have led to novel polymers with impressive device performance in the past five years. This is one of the reasons that Scharber forecasted a 13% efficiency limit of single junction devices within the polymer:fullerene BHJ systems.[40] Indeed, this prediction seems to declare the end of an era where the creative design of conjugated polymers consistently led to increased device efficiency in polymer:fullerene

BHJ solar cells; to support this, in the past five years, the record high efficiency for polymer:fullerene BHJ solar cells has been improving only incrementally (at best). However, please note that this 13% efficiency cap is based on empirical formulations; in fact, there are no fundamental limitations to restrict the efficiency from going beyond 20%.[41] To reach that goal (e.g., 20%), however, the community should explore unconventional, bold, and creative ideas. For example, the increasingly heated research on replacing fullerene with other n-type organic semiconductors in BHJ systems[42] would call for new design rules for both conjugated polymers and these versatile n-type organic semiconductors. In fact, rapid progress has been made in this emerging area, with most recent reports already touting over 12% device efficiency with these fullerene-free systems.[43] A new era is already on the horizon, where molecular engineering will play an even more important role. Furthermore, these non-fullerene based systems not only present new challenges for understanding the morphology and the device physics of these systems, they also – perhaps more importantly – offer opportunities for new discoveries. For example, a recent report demonstrated a non-fullerene based BHJ solar cell where the charge separation required only a very small driving force,[44] a desirable feature reserved for inorganic solar cells in the past. With such a negligible driving force (which is typically over 0.3 eV for polymer:fullerene BHJ solar cells), this cell largely avoided the energy loss and achieved a V_{oc} of 1.11 V out of a band gap of 1.72 eV. It would be curious to see whether such a low V_{oc} loss can be joined with high J_{sc} and FF as well. If this can be successfully implemented, the aforementioned 20% would be within reach more quickly.

Even within the existing polymer:fullerene BHJ systems, many important questions are still waiting to be addressed. For example, it is still hard to distill general correlations among (1) properties of materials, (2) morphological features of the corresponding BHJ thin films, and (3) device physics in BHJ blends, partly because all three are intrinsically correlated (thus convoluted) (Figure 1). On the bright side, a number of qualitative correlations have been established as more BHJ systems are studied in detail; however, it is still almost impossible to make any quantitative correlations. Physical models based on device physics can make useful predictions on the desirable quantity for key parameters (e.g., mobility);[38a,c,45] However, how to reach these desirable quantities via engineering materials and controlling the morphology remains a grand challenge. Nevertheless, as the field is moving forward, all these questions will be better addressed, which will not only help the design of organic materials for solar cells, but also offer invaluable input to other related fields (e.g., polymer field effect transistors) and beyond.

Acknowledgements

S.X. was supported by National Natural Science Foundation of China (NSFC, 21673170). Q.Z. and W.Y. were supported by National Science Foundation (DMR-0954280, and DMR-1507249), and Office of Naval Research (Grants N000141410221).

Received: March 11, 2016
Revised: November 13, 2016
Published online: December 30, 2016

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